

LA-UR-21-22658

Approved for public release; distribution is unlimited.

Title: Total Moisture Analysis of Salts by Dissolution

Author(s): Stein, Benjamin
Lam, Nhu Huynh

Intended for: Report

Issued: 2021-03-18

Disclaimer:

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by Triad National Security, LLC for the National Nuclear Security Administration of U.S. Department of Energy under contract 89233218CNA000001. By approving this article, the publisher recognizes that the U.S. Government retains nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

Report: *Total Moisture Analysis of Salts by Dissolution*

Sample preparation - Mila Lam

Experimenter - Mila Lam

Data analysis - Mila Lam, Benjamin W. Stein

Abstract

This report discusses recent efforts within TA-48 in developing a robust, defensible, and straightforward procedure for determining the moisture content of alkali and alkaline metal halide salts utilizing a total dissolution Karl-Fischer titration method. Utilizing statistical analysis of blank and dissolved salt samples, we determine a (3 sigma) *detection limit* of 67 micrograms H₂O/g salt, and a (10 sigma) *quantification limit* of 160 micrograms H₂O/g salt. Several salts are analyzed, and suggestions for future efforts are given.

Discussion

In this experiment, we were interested in determining the total amount of moisture in the salt samples, including water of crystallization, entrapped water, and adherent moisture. A complete sample dissolution was necessary to release the total water content in these samples¹⁻³, so a solvent extraction method was chosen over the common Karl-Fischer oven method. Since salts dissolve very slowly in Karl-Fischer reagent (Coulomat A, methanol based), “dry” formamide as a solubilizer is recommended for inorganic salts¹⁻³. This external extraction using “dry” formamide does not require high temperature and also avoids decomposition or side reactions of samples at high temperature as in the Karl-Fischer oven method.

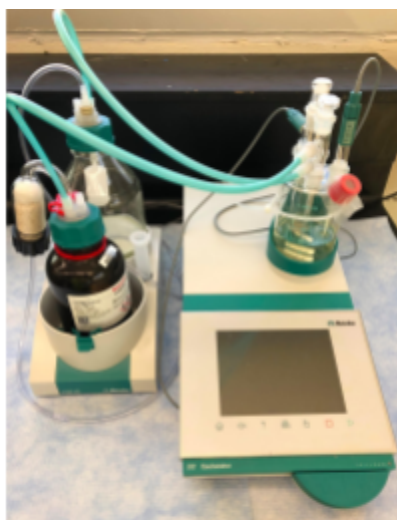


Figure 1: Karl-Fischer titration instrument (Metrohm Ti-Touch 917 Coulometer) in 48-0001-606 (alpha wing).

Table 1. Average moisture content (ppm) of 1 mL “dry” formamide blank from 3 different days measurements. Errors in parentheses are one standard deviation.

| Day | Average mass of blank aliquots (g) | Moisture content of blank aliquot (ppm) |
|---------|------------------------------------|---|
| 1 | 1.20 (0.04) | 136 (1) |
| 2 | 1.23 (0.02) | 143.1 (0.8) |
| 3 | 1.19 (0.04) | 147 (1) |
| Average | 1.21 (0.06) | 142 (2) |

Table 2. Average moisture content (ppm) of the 1 mL extracted “wet” NaCl sample aliquots from 3 different days measurements. Errors in parentheses are one standard deviation.

| Day | Average mass of NaCl extracted aliquot (g) | Moisture content before subtracting blank (ppm) | Moisture content after subtracting blank (ppm) |
|---------|--|---|--|
| 1 | 1.27 (0.03) | 184.76 (2.06) | 45 (2) |
| 2 | 1.27 (0.04) | 189.18 (4.98) | 43 (5) |
| 3 | 1.26 (0.03) | 197.08 (1.37) | 47 (1) |
| Average | | 190.34 (5.57) | 45 (5) |

The moisture measurements of “dry” formamide blanks and “wet” NaCl samples were conducted in three different days to check reproducibility of data as well as to see how much surrounding environments affected data collection day by day (Figure 1). The moisture content of blanks and NaCl samples are summarized in Table 1 and 2. The Hydranal dry formamide from Honeywell was received with maximum 0.02% H₂O (200 ppm). In every 1 mL aliquot, the average moisture content of “dry” formamide blanks measured on 3 different days was 141.97 ± 1.82 ppm. The average moisture content in the “wet” NaCl extracted aliquots (before subtracting blanks) measured from 3 different days was 190.34 ± 5.57 ppm. Using Eq. 1, the average moisture content of extracted “wet” NaCl in every ~1 mL aliquot (after subtracting blanks) was calculated to be 45.23 ± 5.13 ppm. In other words, in every 1 mL extracted NaCl sample aliquot, 73.96 mg of NaCl has a moisture content of approximately 45 ± 5 ug, giving an final moisture content (in the solid salt) of **610 ± 70 ppm**.

In order to determine whether there is a statistically significant difference between the blank and salt sample, a *t-test* was performed to compare the moisture content of blank mean value to the moisture content of salt aliquot mean value (before subtracting blank)⁴. The *t-test* at 95% confidence level showed that $t(\text{calculated}) > t(\text{table})$ indicating the moisture contents of blank and NaCl extracted aliquot (before subtracting blank) are considered to be significantly different.

When the moisture content of blank is 142 ppm, the lowest moisture content in the NaCl extracted aliquot (**before** subtracting blank) we can reliably measure at the detection limit (LOD) is calculated to be 147 ppm (blank + 3σ) using Eq. 2. In other words, in a 1 mL aliquot, the detection limit would be an additional 5 ppm of moisture added from the salt. For an 1 mL aliquot containing 75 mg of NaCl, this corresponds to a detection limit of **~67 ppm** (dry salt weight basis). The limit of quantification (LOQ) which is the lowest moisture content in the NaCl extracted aliquot at which a measurement is quantitatively meaningful is calculated to be **160 ppm** (10σ) using Eq. 3.

Attempts to achieve a better detection limit of moisture content of sample were done by letting the formamide stand over activated 3Å molecular sieves under inert atmosphere. Loadings of 20 % and 30 % (w/w) of sieves were examined over a certain number of hours to achieve low ppm levels (Table 3). The relative standard deviation of all measurements were within 10 % error. Optimum drying is obtained with soaking of formamide over 30% w/w 3Å molecular sieves for 2 hours, by which time the water content reduces to about 38 ppm. Hence, the lowest moisture content of NaCl which is likely to be reliably distinguished from the blank (LOD) and the lowest moisture content of NaCl with acceptable precision and accuracy under the experimental conditions (LOQ) are calculated to be 41 ppm and 48 ppm, respectively. The determination of moisture content of dried KCl and LiCl/KCl salts were performed using the above procedure and reported in Table 4. Despite this large reduction in blank moisture content, the standard deviation of the measurements *was not affected*. This suggests that the standard deviation of ~1-5 ppm is an absolute instrumental error. Improving the detection limit therefore depends upon the mass of salt that is introduced into the titrator.

Table 3. Dehydration of formamide over activated 3Å molecular sieves under inert atmosphere.

| Time in sieves (hr) | 20 % w/w | | | 30 % w/w | | |
|------------------------|------------------|---------------------|-------------------------|------------------|---------------------|-------------------------|
| | Formamide (g) | µg H ₂ O | ppm H ₂ O | Formamide (g) | µg H ₂ O | ppm H ₂ O |
| 0 | 1.22 | 170.1 | 139.4 3 | 1.22 | 170.1 | 139.43 |
| 1 | 1.12 | 103.6 | 92.5 | 1.11 | 108 | 97.29 |
| 2 | 1.12 | 77.5 | 69.19 | 1.16 | 45 | 38.79 |
| 3 | 1.2 | 61.9 | 51.58 | 1.17 | 95 | 81.19 |
| 5 | - | - | - | 1.12 | 152.5 | 136.16 |
| Overnight | 1.15 | 240.9 | 209.4 7 | - | - | - |

Table 4. Average moisture of KCl and LiCl/KCl salts (dried in the oven overnight at 275 °C) in 1 mL dehydrated formamide aliquot under inert atmosphere. Three replicates were performed for each salt. Errors in parentheses are one standard deviation.

| KCl | | | | | |
|-----------------------|--|--------------------------|-------------------------|------------------------------------|--------------------------------|
| Blank formamide (ppm) | Average mass of 1 mL KCl extracted aliquot (g) | Before subtracting blank | After subtracting blank | Amount of KCl in 1 mL aliquot (mg) | H ₂ O content (ppm) |
| 32 (2) | 1.07 (0.02) | 38 (7) | 5.8 (0.2) | 59 (1) | 107 |

| LiCl/KCl | | | | | |
|-----------------------|---|---------------------------|--------------------------|---|--------------------------------|
| Blank formamide (ppm) | Average mass of 1 mL LiCl/KCl extracted aliquot (g) | Before subtractin g blank | After subtractin g blank | Amount of LiCl/KCl in 1 mL aliquot (mg) | H ₂ O content (ppm) |
| 32 (2) | 1.15 (0.01) | 36.83 (6) | 4.5 (0.2) | 67.69 (0.47) | 77 |

Recommendations for future measurements

1. Measure moisture content of other salts from TA-59/TA-55 and compare with their results.
2. Consider oven-based measurements to compare total vs. adherent moisture content.

Experimental

Karl-Fischer Titration Measurements. All data was collected on a Metrohm 917 Coulometer with generator electrode with diaphragm located in Alpha Wing (48-0001-606). The instrument is capable of measuring data in the range of 10 µg to 200 mg absolute water. The catholyte and anolyte reagents used for the measurements were Hydranal Coulomat CG (5 mL) and Hydranal Coulomat A (100 mL), respectively, purchased from Honeywell Fluka. Hydranal dry formamide was purchased from Honeywell Fluka and used as received. Sodium chloride (NaCl) was purchased from Sigma Aldrich (ACS reagent, ≥ 99.0%). Some amount of NaCl was ground into a fine powder using mortar and pestle and then stored in an argon glove box. The experiment was carried out in 3 different days with one salt vial for each day. Each salt vial was sampled at least 4 - 5 times for that day. Prior to titration of the salt samples, titration of dry formamide as a blank was done. The blank measurements were repeated three times for each day. For

preparation of the blank, a 1 mL dry formamide sample was loaded in a 1.0 mL gas-tight syringe (Hamilton, catalog # 81320) capped with a septum in an argon glove box. After preliminary titration and stabilization of drift, the blank was injected into the titration cell. The exact sample weight was determined by weighing the syringe before and after injection. For preparation of salt sample, each day, a 1 g NaCl was weighed out in a 20 mL glass scintillation vial and dissolved completely in 12 mL dry formamide (Hydranal, catalog # 34724-1L) on a stirring hot plate at 30 °C for about 1 - 2 hours. The exact masses of NaCl and dry formamide used were recorded. Once the solution was cooled down, a NaCl extracted aliquot (1 mL) was loaded and titrated in the same manner as for the blank. The water determination of NaCl extracted aliquot was calculated in ppm corrected for the blank value of the dry formamide solvent using Equation 1. For all experiments, the stirring time was 60 seconds; the titration time was 180 seconds.

The water content (X) of the salt extracted sample (in ppm) can be calculated as:³

$$X = \frac{10^6}{10^6 - C} \left[C \frac{a}{b} - B \frac{a}{b} \right] \quad (\text{Eq. 1})$$

where C is the measured water content of the supernatant extraction solvent in ppm, B is water content of blank/solvent in ppm, *a* is amount of solvent in grams, and *b* is amount of sample extracted with solvent in grams.

The limit of detection (LOD) is defined as the lowest analyte concentration likely to be reliably distinguished from the blank and can be calculated as:^{5,6}

$$LOD = \text{mean}_{blank} + 3\sigma_{blank} \quad (\text{Eq. 2})$$

The limit of quantification (LOQ) is defined as the lowest analyte concentration that can be determined with acceptable precision and accuracy under the experimental conditions and can be calculated as^{5,6}:

$$LOQ = \text{mean}_{blank} + 10\sigma_{blank} \quad (\text{Eq. 3})$$

References

1. Water Determination by Karl Fischer Titration [PDF File]. (2006). *Metrohm Ltd.* Retrieved from www.metrohm.com.
2. Water Determination by Karl Fischer Titration [PDF File]. (2016). *Honeywell International Inc.* Retrieved from www.lambda.sk.
3. Good Titration PracticeTM in Karl Fischer Titration [PDF File]. (2011). *Mettler Toledo.* Retrieved from www.mt.com.
4. Harris, D. C. (2003). Statistics. In Fiorillo, J.; Rossignol, R.; Byrd, M. L.; McCorquodale, A. (Eds.), *Quantitative Chemical Analysis* (6th ed., pp. 61-75). Macmillan.
5. Kirchner, C. J. (1988). Estimation of Detection Limits for Environmental Analytical Procedures. In Currie, L. A. (Ed), *Detection in Analytical Chemistry: Importance, Theory, and Practice*. American Chemical Society.

6. Shrivastava, A.; Gupta, V. Methods for the Determination of Limit of Detection and Limit of Quantitation of the Analytical Methods. *Chron Young Sci* **2011**, 2 (1), 21.